



A review of hydrothermal biomass processing



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ABSTRACT

Hydrothermal processing is an important thermochemical conversion process that is used to convert biomass into valuable products or biofuel. The process is usually performed in water at 250–374 °C under pressures of 4–22 MPa. The biomass is degraded into small components in water. Based on the target products, i.e., bio-oil, bio-gas or bio-carbon, the process conditions (temperature, pressure and time) are chosen. There has been significant effort in evaluating various biomass resources for hydrothermal processing because the process is suitable for any type of biomass including the co-utilization of biomass with waste materials. Additionally, because most biomass resources have high moisture contents, the most efficient way to process them is through hydrothermal processing. To understand hydrothermal biomass processing and the degradation pathway of biomass, it is necessary to understand the properties of water under hydrothermal conditions (i.e., subcritical and supercritical). In this respect, the physicochemical properties of water under subcritical and supercritical conditions and the interactions of water with biomass are discussed in the present paper.

This review focuses on the hydrothermal processing of biomass and identifies the characteristics of various types of hydrothermal processing products. Additionally, this review provides an overview of the available biomass, the use of biomass as an energy source and related conversion technologies.

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1. Introduction

As a result of an increasing world population and rapidly evolving industries, energy demand is constantly increasing. Since the industrial revolution, the consumption of fossil fuels, such as

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oil, coal, and natural gas, has increased and caused significant environmental pollution. As a result of the use of fossil fuels, environmentally harmful gases such as CO, CO₂, NO_x, SO_x, CH₄, which have been linked to the greenhouse effect and global warming, have been released into the atmosphere. Global warming is mostly considered to be CO₂-induced based on the effect-linked increase in the concentration of CO₂ [1]. Unless the amount of CO₂ released into the atmosphere is controlled, global warming and the resultant climate change are expected to become inevitable and to threaten the future of the planet. The search for alternative energy sources has gained great importance because the use of fossil fuels is harmful to the environment and their supply is limited, as evidenced by the world's rapidly declining oil reserves [2].

Biomass is a term that encompasses all living or recently passed creatures and their wastes. As an alternative to fossil fuels, biomass has a high utilization potential and is one of the most important energy sources of the future [3,4]. One of the advantages of biomass is that it is a clean energy source. CO₂, taken from the atmosphere by plants through photosynthesis, is utilized by the plant as a source of energy and returned to the atmosphere without additional CO₂ release. Another advantage of biomass is that it is renewable. The formation of fossil fuels takes millions of years, while plants used as a source of biomass grow in periods of months or years. Plants can be directly used as a source of biomass or as various raw materials with low economic value, such as plant-based waste, industrial waste, household waste, and animal waste. Significant progress, especially in developed nations, has been made in obtaining fuel from biomass. Applications, such as the production of ethanol from corn and biodiesel from oil crops like canola or waste oils, are rapidly increasing.

Hydrothermal processing, also known as "Hydrothermal Upgrading (HTU[®])", is a biomass conversion technology introduced by the Shell Oil Company in the 1980s. In this method, the thermal degradation of biomass takes place in water and affects the physicochemical properties of water [5]. For example, its dielectric constant is reduced at high temperatures. Therefore, while organic substances are insoluble in water under normal conditions, water can become a good solvent for non-polar substances under supercritical conditions. An increase in the ionic character of water can facilitate acid–base-catalyzed reactions [6]. Additionally, most biomasses contain significant amounts of moisture. Raw materials must first be dried if the hydrothermal method is not used. This requires additional costs in industrial applications. For these reasons, the conversion of biomass into precious products by hydrothermal processing is a major subject of research.

This review examines the liquefaction of biomass by hydrothermal processing, the separation of resulting products and the characterization of liquid products. In addition, biomass, biomass components and biomass conversion technologies are reviewed.

2. Biomass

Biomasses are organic substances mainly composed of carbon, hydrogen and oxygen, are living or have recently lived in the world, and have solar energy stored in its molecular bonds. Biomass has a high utilization potential among renewable energy resources. Examples of biomass include plants, such as trees, algae, corn, wheat, rye straw, grass, and fruit, vegetable wastes, plant-based waste, urban waste and agro-industrial waste [7–11].

2.1. Using biomass as an energy source

Alternative energy sources include biomass, wind, solar, geothermal and hydroelectric power [12]. Biomass has always been a major source of energy for mankind; it accounts for 10–14%

of worldwide energy demand. However, by 2050, it is projected that the worldwide supply of oil reserves would be exhausted and nearly half of the global energy demand would be supplanted by biomass [3,13]. Biomasses are commonly used as electrical/thermal energy, as fuel for transportation and as raw materials for the production of chemicals; the applications for biomass continue to grow and are increasing rapidly [3]. Although there are areas where biomass is effectively used, it is inefficiently utilized in direct combustion, especially in less-developed countries. However, the amount of atmospheric pollution generated remains negligible compared with other pollution sources of energy production [13]. A wide variety of studies has been conducted on the use of biomass as a source for renewable energy and an alternative to fossil fuels; interest in biomass continues to grow in an increasing trend [14–18]. The moisture content, calorific value, fixed carbon and volatile matter content, ash and residual contents, alkali metal content and cellulose/lignin ratio play important roles in the selection of a biomass as an energy source [3]. The amount and type of energy obtained vary according to properties of the selected biomass and the applied conversion technology. Biomass can be directly used in combustion processes in order to obtain heat or to generate electricity [19]. Products obtained from biomass gasification processes are generally used to generate heat or electricity in an engine or turbine. Solid and liquid products resulting from pyrolysis and liquefaction processes can be used as fuel after various improvements. Biogas obtained as a result of the biochemical degradation process of biomass can be used as fuel or to generate electricity in engines. In developed countries, there is an increasing trend in the use of bioenergy as an alternative energy in handling and transportation sectors. There has been significant progress in the conversion of vegetable oil and animal fat into biodiesel as an alternative to petroleum-based diesel fuels. Biodiesel fuel can be produced by the transesterification of oils [19,20]. Oils obtained from plants, such as soybean, canola, corn, and rapeseed, are the most widely used raw materials for biodiesel production.

2.2. Components of biomass

A biomass is any heterogeneous mixture of organic substances and a small amount of inorganic substances. Cellulose, hemicellulose, lignin, and extractives are the main components of lignocellulosic materials. Algal biomass mainly constitutes lipids, carbohydrates and proteins. The amount of each component in biomass varies according to the type of biomass, tissue type, growth stage and growing conditions of the plant [21,22]. Biomass has a high oxygen content compared with fossil fuels. Typically, by biomass dry weight, 30–40% is oxygen, 30–60% is carbon and 5–6% is hydrogen depending on the ash content. Nitrogen, sulfur and chlorine make up less than 1% of the biomass and can be found in the structure of some types of biomass [22]. Elements of biomass, in the order of decreasing prevalence, are C, O, H, N, Ca, K, Si, Mg, and Al [21]. Inorganic components of the biomass are contained in the ash. The carbohydrate portion of biomass is composed of cellulose and hemicellulose, whereas the non-carbohydrate portion is composed of lignin [2]. Cellulose and hemicellulose provide structural and mechanical strength to the plant, while lignin, a non-carbohydrate, maintains the stability of these structures [23].

2.2.1. Cellulose

Cellulose is the most abundant natural polymer with an estimated annual worldwide production of 1.5×10^{12} t and is considered to be a nearly inexhaustible source of raw biomass material [24,25]. Cellulose, represented by the general formula (C₆H₁₀O₅)_n, is a long chain polysaccharide with a high degree of

polymerization (approximately 10,000), a high molecular weight (approximately 500,000) and is formed by the β -1,4 glycosidic linkage of D-glucopyranose units. Cellulose is insoluble in water at room temperature but is partially soluble at 302 °C and completely soluble at 330 °C under subcritical water conditions [26]. Due to its tight fiber structure formed by hydrogen bonding, cellulose is insoluble in most solvents [27]. Fig. 1 shows the structure of cellulose.

2.2.2. Hemicellulose

Hemicellulose forms approximately 20–30% of the dry weight of most wood species. It is an amorphous heteropolysaccharide and has a lower degree of polymerization than cellulose. It is formed by the high degree branching of a straight-chain skeleton composed mainly of xylan and glucomannan [23,28]. Although the structure of hemicellulose varies depending on the biomass source, it primarily contains D-glucopyranose, D-galactopyranose and D-mannopyranose monomers, L-arabinofuranose, and D-xylopyranose monomers [29]. These units are shown in Fig. 2. Other than arabinose, which is in L-configuration and furanose form, all monosaccharides are in D-configuration and pyranose forms. The degree of polymerization is approximately 100–200 sugars per hemicellulose molecule [29]. In general, the amounts of hemicellulose in wood and woody biomasses are greater than those in herbaceous and agricultural biomasses [30]. Hemicellulose, which forms hydrogen bonds with cellulose, forms covalent bonds with lignin (primarily α -benzyl ether bonds), and ester bonds with acetyl units and hydroxycinnamic acids [29]. Hemicellulose is more unstable than cellulose and therefore, degrades more easily when subjected to heat treatment. The molecular structure of a typical hemicellulose, xylan, is shown in Fig. 3.

2.2.3. Lignin

Lignin, a natural polymer, is an aromatic compound in which phenylpropane units, with hydroxyl and methoxy groups, are linked primarily through ether bonds [31]. Fig. 4 shows structures of three basic monomers of lignin. Lignin makes up 18–25% of hardwoods and 25–35% of softwoods [28]. Lignin is an amorphous material, hydrophobic, and its solubility in water is very low. Plants use lignin to help strengthen their structure, regulate the flow of fluids, protect against micro-organisms and store energy [28,32]. Lignin is the basic binder of fibrous components in plants [30]. Woody plants are composed of tightly bound fibers, and thus, their lignin contents are higher than herbaceous plants, which are composed of loosely bound fibers. The chemical structure of a

fragment of a lignin polymer is shown in Fig. 5. Compared with other bioorganic compounds, lignin is more resistant to natural decay and biological degradation. Due to the higher energy content of lignin compared with those of cellulose and hemicellulose, lignin content provides a biomass with a higher heating value [30]. Lignin structure has a significant impact on product yields and products during hydrothermal processing. Phenolic compounds with ethyl and methyl groups are the primary compounds produced from the degradation of lignin [31].

2.2.4. Extractives

Extractive substances are a group of heterogeneous substances which can be extracted from biomass by various polar or non-polar solvents [33,34]. They are composed of a wide range of organic and inorganic compounds, including proteins, fats, fatty acids, sugars, phenols, terpenes, resin acids and resin. The type and amount of these components vary with the type of plant. Although extractives are small components that typically make up less than 2% of the dry weight of plants, they are important contributors to certain characteristics of the plant, such as color, smell, taste and durability [28,33]. Extractives can also be classified as water soluble, toluene–ether soluble or ether soluble according to the solvent used to extract them [28]. Herbaceous plants have a higher amount of extractive matter than woody plants. Rapeseed, soybean plants, corn grains, and sugar cane contain high amounts of extractive components [30].

3. Biomass conversion technologies

Technologies used to convert biomass into either bio-fuels (i.e., solid, liquid, and gas fuels) with high energy content or valuable

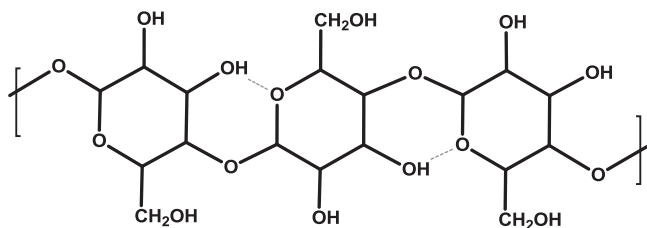


Fig. 1. Structure of cellulose.

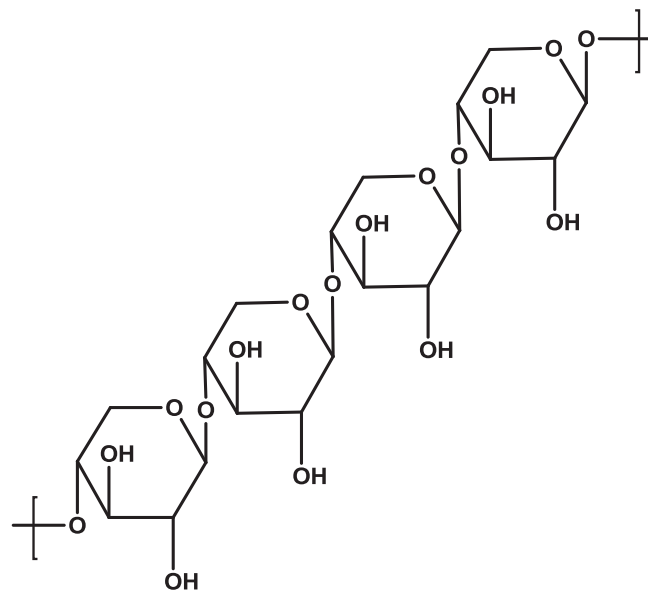


Fig. 3. Molecular structure of xylan.

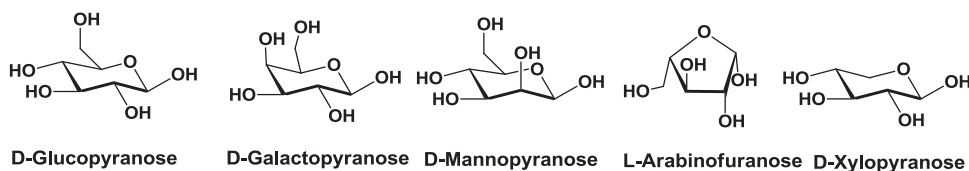


Fig. 2. Basic constituents of hemicellulose.

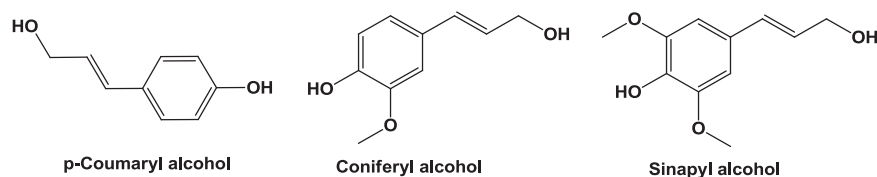


Fig. 4. Basic monomers of lignin.

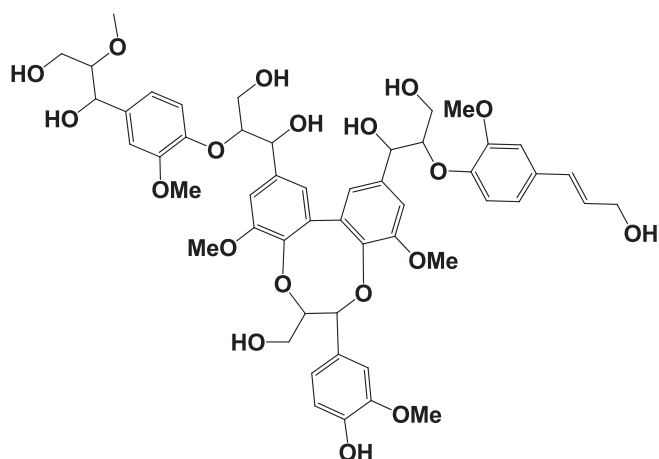


Fig. 5. Structure of a sample fraction of lignin.

the product obtained from fermentation is liquid. The conversion of starch and sugar-based raw materials into bio-ethanol by fermentation is used for commercial purposes. However, the degradation of lignocellulosic biomass, such as wood into sugars, is a difficult and expensive process. Typically, a hydrolysis pre-treatment is used to convert cellulose and hemicellulose into sugars; the use of fermentation to degrade lignocellulosic biomass increases the processing cost and is commercially not preferred [36].

3.2. Thermochemical conversion technologies

Thermochemical conversion technologies are based on the thermal breakdown of biomass into fuels and valuable chemicals. The thermochemical conversion of biomass is one of the oldest processes humanity has exploited for a variety of purposes, including heating, cooking and the production of coke. Thermochemical conversion technologies include pyrolysis, hydrothermal processing, combustion, and gasification [6]. The combustion technology for biomass is the oldest known and most widely used thermochemical conversion method. In this process, thermal energy is obtained as a result of the rapid reaction between fuel and oxygen. Combustion technology is widely used in vehicles and factories. Gasification is the process in which biomass is converted into gas fuel or synthesis gas containing varying amounts of H_2 , CO , CO_2 and CH_4 . In this process, a gasification agent, such as steam, air, CO_2 , O_2 or their mixtures, is required [37]. Oxygen is the most widely used active agent. In gasification, energy is stored in the chemical bonds of the gas product, whereas in combustion, energy is released as chemical bonds are broken [36]. During gasification, oxygen from the raw material is removed via decarboxylation or dehydration, and a gas product with a high H/C ratio is obtained. If the oxygen content in the gasification media exceeds a certain value, the process changes from gasification to combustion.

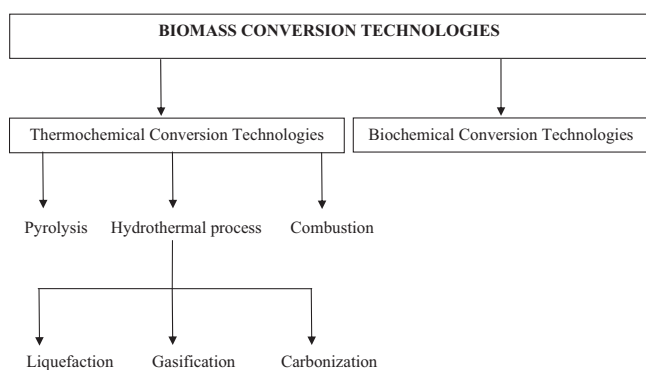


Fig. 6. Biomass conversion technologies.

chemicals can be classified under two groups. The first group, biochemical conversion technologies, degrades biomass with enzymes and microorganisms. The second group, thermochemical conversion technologies, degrades biomass with heat. Hydrothermal processing is a thermochemical conversion technology and is utilized in the production of liquid, gaseous and solid products from biomass. Biomass conversion technologies are shown in Fig. 6.

3.1. Biochemical conversion technologies

The degradation of biomass by biochemical processes occurs naturally. These processes, which include aerobic and anaerobic degradations, fermentation, and enzymatic hydrolysis, are performed by bacterial enzymes and micro-organisms [35]. In anaerobic degradation, which is carried out by bacteria using oxygen from the biomass instead of oxygen from air, CH_4 and CO_2 gases and a solid product are generated [36]. In aerobic degradation, micro-organisms break down biomass to produce CO_2 , heat, and a solid product, using oxygen from air. The process in which yeast converts biomass into sugar and subsequently ethanol and other chemicals is called fermentation. Unlike anaerobic degradation,

3.2.1. Pyrolysis

Pyrolysis is the thermal degradation of an organic substance in an inert atmosphere. Pyrolysis is an important technology because the resultant liquids from the pyrolysis of biomass can be easily handled, stored and transported [38,39]. Inert gases, such as nitrogen and argon, are usually used to remove oxygen from the pyrolysis environment. As a result of pyrolysis, liquid, solid and gaseous products are obtained. The amount and content of these resulting products vary depending on various parameters. From the pyrolysis of biomass, a condensable gas (liquid) and a non-condensable gas (primary gas) are generated. The condensable gas product comprises heavy molecules and is known by common names as pyrolytic oil, tar, and bio-oil. The liquid product has a black tarry structure and is formed from the decomposition of cellulose, hemicellulose and lignin in the biomass. The content of the liquid product includes oxygenated hydrocarbons, such as phenolic ethers, alkyl phenolics, heterocyclic ethers, and polyaromatic hydrocarbons, and a significant proportion of water [40]. Water is formed both from the moisture in the biomass and decomposition reactions of pyrolysis. Some of the compounds present in biomass may remain undecomposed after pyrolysis and

be mixed with the final liquid product. Gases with lower molecular weights, such as CO₂, CO, CH₄ and H₂, do not condense during cooling and are recovered as gas products. Furthermore, volatiles (liquids and gases) and solid products are obtained from the primary decomposition of the solid and the secondary reactions of volatiles [40]. The solid product, called char, mainly contains carbon, hydrogen and oxygen. The inorganic matter content of char is less than that of fossil fuels [40,41]. The solid product can typically be used as a fuel or as a precursor in the production of activated carbon [42].

The products obtained as a result of pyrolysis vary depending on several factors, such as biomass type, pyrolyzer design, heating rate, pyrolysis temperature, residence time, and the presence of a catalyst. The structure of biomass is one of the more important factors that determines the composition of the pyrolysis products [40]. The decomposition temperature of each of biomass components is different. For example, hemicellulose, one of three essential components of lignocellulosic biomass, decomposes at approximately 220 °C; lignin decomposes for a range of temperatures from 200–500 °C; and cellulose decomposes at approximately 280 °C [43]. Another important factor is the pyrolysis temperature, which significantly affects the product quantities. As the temperature increases, the amounts of liquid and gaseous products also increase because of the increasing number of decomposed components [41]. The size and shape of particles used may indirectly influence the heating rate, causing variability in product differentiation. Gases released by small biomass particles may spread to the pyrolysis environment and decompose for a second time. Larger particles may prevent the release of such gases, thereby increasing the amount of solid product [35,41].

3.2.2. Hydrothermal processing

Hydrothermal processing is an important thermochemical conversion process used to convert biomass into valuable products or biofuel. Hydrothermal liquefaction and gasification are two basic types of hydrothermal processes. Hydrothermal carbonization is a relatively new method and has gained prominence in recent years [44–46].

A hydrothermal process is usually performed in water at 250–374 °C under a pressure of 4–22 MPa. The process can also be carried out under self-generated pressure. One of the most important advantages of this procedure is that it can use biomass with high moisture content without the need for pre-drying [6,37]. The application of hydrothermal gasification to biomass with a moisture content of at least 30% under supercritical conditions requires less energy than that required for pre-drying the biomass [31]. Therefore, it is an appropriate process for the utilization of biomass wastes with high moisture contents generated by the agriculture and food industries and plants such as algae. The hydrothermal process can also be carried out at low temperatures and removes oxygen from biomass. Additionally, potential phase shifts can be prevented by performing the process under pressure resulting in increased process yields [47]. Life cycle analysis (LCA) is very important in order to assess the benefits of hydrothermal processing of biomass. Previous studies concerning life cycle analysis (LCA) analysis of hydrothermal algal biomass showed that the process can be a viable and economic option. However, the aqueous phase and byproducts should be used effectively. The aqueous phase can be used in either gasification or cultivation medium for biomass [48,49]. The byproducts can be used in the production of electricity and process heat, as well as the recovery of inherent nutrients [50]. Besides the benefits of hydrothermal biomass processing, there are also some disadvantages. The method requires large water handling equipment and capabilities [6], typically uses more complex and expensive reactors [51], and is difficult to manage the separation and extraction

procedures at the industrial scale. Additionally, it is difficult to calculate the gas yield because of a complex mass balance due to variability in the hydrothermal media [52,53].

The hydrothermal process is divided into two reaction conditions: subcritical and supercritical water conditions. These two conditions are determined by the critical point of water (i.e., 374 °C and 22.1 MPa). For each condition, water has different characteristics [6,54]. These conditions have their distinct advantages. For example, most biomass components such as cellulose and lignin are insoluble in ambient water, but are soluble in high temperature water or supercritical water. Under supercritical conditions, macromolecules in the biomass are broken down to their basic building blocks to yield gaseous products. Under conditions with a lower temperature and pressure, macromolecules are broken down to form a viscous bio-oil product [31]. The decomposition steps of biomass during the hydrothermal process can be summarized as follows: at approximately 100 °C, the water-soluble portion of the biomass disperses into water, and hydrolysis takes place above 150 °C. Meanwhile, biomass polymers, such as cellulose and hemicellulose, disintegrate into their monomeric chains. At approximately 200 °C and 1 MPa, solid biomass becomes slurry. Finally, at approximately 300 °C and 10 MPa, liquefaction occurs and the oily product is obtained [37].

In a hydrothermal process, biomass is converted into a solid product called bio-char, a liquid product called bio-oil and a gas product. Fig. 7 shows the products from the hydrothermal conversion of biomass. Biomass can be converted into the target product (i.e., bio-oil, bio-char and gaseous products) by changing process variables such as reaction temperature, reaction time, catalyst presence, and reactor pressure [37]. Bio-oil is a hydrophobic organic liquid with a reduced oxygen content and a high energy density [31]. It may contain hundreds of compounds depending on the nature of the raw material and experimental conditions. This liquid product can replace heavy petroleum oil and be directly used as fuel for co-firing with coal or converted into high-quality distillate fuels, such as diesel and gasoline. Because hydrocarbons with high oxygen contents have lower energy contents, higher melting points, higher boiling points and greater viscosities than other hydrocarbons with the same molecular weight, the oxygen content of bio-oils can be reduced by decarboxylation and hydrodeoxygenation reactions to improve the quality of the fuel [31]. It is also possible to obtain valuable chemicals from bio-oils by various purification and separation methods.

3.2.2.1. Subcritical and supercritical water. For water, the critical point occurs at 374 °C and 22.1 MPa. Subcritical water is classified below the critical point at a 100–374 °C temperature range and under sufficient pressure to remain liquid [55]. Supercritical water occurs when the temperature is above 374 °C and the pressure is above 22.1 MPa [56]. Subcritical and supercritical water have several advantages because of their various properties. Solvent properties of water can be changed as a function of temperature and pressure [6]. Near the critical temperature, the ionic product of water is greater than that of room temperature; water can be an effective medium for acid–base-catalyzed organic reactions under critical conditions. The viscosity of water decreases with increasing temperature and has a value close to the viscosity of water vapor near the critical point. A low viscosity provides a high diffusion coefficient, leading to high reaction rates. In addition, water at high temperatures can also behave as a reactant in the hydrothermal reaction medium [57]. Under hydrothermal conditions, water molecules may participate in hydrolysis reactions and can act as a hydrogen source [58,59].

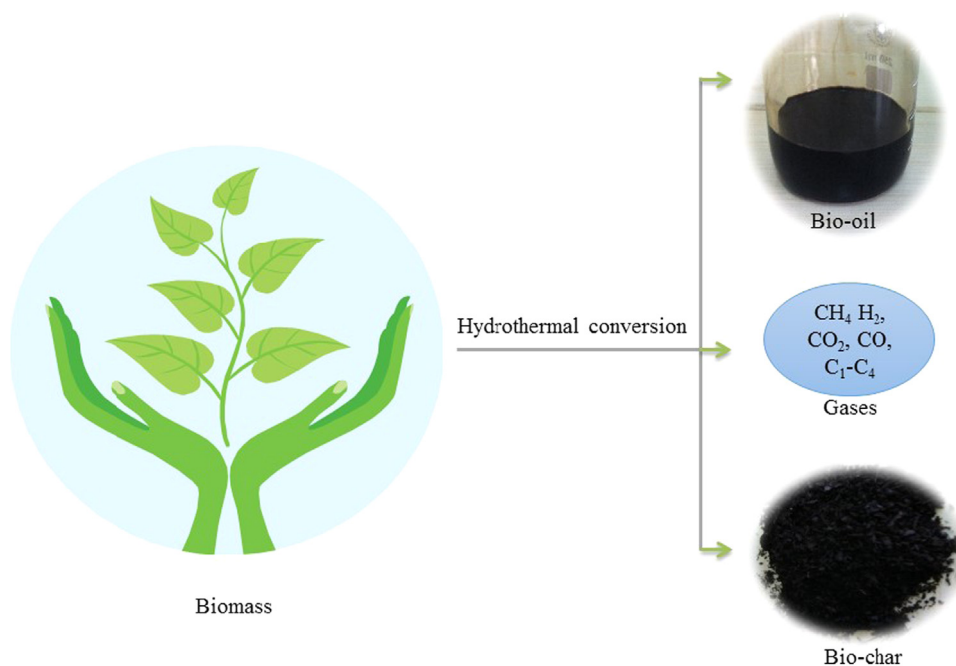


Fig. 7. Products obtained from hydrothermal conversion of biomass.

Table 1
Physicochemical properties of water as a function of temperature and pressure [56].

	Ambient water	Sub-critical water	Super-critical water	
Temperature, T (°C)	25	250	400	400
Pressure, p (MPa)	0.1	5	25	50
Density, ρ (g cm ⁻³)	0.997	0.80	0.17	0.58
Dielectric constant, (ϵ)	78.5	27.1	5.9	10.5
pK_{su}	14.0	11.2	19.4	11.9
Heat capacity, c_p (kJ kg ⁻¹ K ⁻¹)	4.22	4.86	13	6.8
Viscosity, μ (mPa s)	0.89	0.11	0.03	0.07
Thermal conductivity, λ (mW m ⁻¹ K ⁻¹)	608	620	160	438

The physicochemical properties of subcritical and supercritical water as a function of the temperature and pressure are shown in Table 1 [56]. Ambient water has a high dielectric constant ($\epsilon \approx 80$) due to the effect of hydrogen bonds, while its dielectric constant decreases ($\epsilon \approx 5$) if it is heated up to the critical point. This decrease in the dielectric constant of water changes the solvent characteristics of water [57]. However, as water approaches its critical point, its properties, including vapor pressure, density, and surface tension, also rapidly change. For example, at the critical point, the vapor pressure of water is 22.1 MPa, while its density decreases to 0.31 g/mL [6].

The hydrothermal conversion of biomass can be controlled by changing the temperature and pressure. While liquefaction processes are generally conducted under 4–20 MPa and 200–370 °C, catalytic gasification can be carried out at temperatures up to 500 °C. Homogeneous gasification can be carried out at temperatures above 500 °C [47]. Other than the hydrothermal process, supercritical water has two widespread industrial applications: the use supercritical water for a power generation cycle, and the use of supercritical water oxidation for removing toxic compounds from organic and biological waste. This method is based on the treatment of water, oxygen and organic compounds with any

heteroatom, such as N, S, P, and Cl, under supercritical water conditions. In principle, this method is a more effective and environmentally friendly application in comparison with many waste treatment practices, such as incineration and selective absorption. No additional energy is required to dry waste materials, and the process occurs inside a completely closed system. Thus, the resulting products can fully decompose and no polluting gas is released [47].

3.2.2.2. Hydrothermal liquefaction. In hydrothermal liquefaction, biomass is converted into liquid products with high energy content. It is usually carried out at high pressure and subcritical water conditions, and an organic liquid called bio-oil is obtained [6,31,60]. This process is similar to the geological formation of fossil fuels. However, fossil fuels are formed by the exposure of biomass to high temperatures and pressures underground for many years, whereas in the case of hydrothermal liquefaction, liquid fuel is obtained within time periods expressed in hours, even minutes [61].

Hydrothermal liquefaction is attractive for a number of reasons: water is a unique and environmentally friendly solvent; the process is suitable for wet biomass (hence, no requirement for biomass drying) and can be conducted at temperatures lower than those used for pyrolysis; finally, the process offers high energy efficiency [47,62,63].

Many complex reactions take place during the transformation of biomass into crude oil-like products. The complexity of the chemical reactions which occur during hydrothermal liquefaction is due to the complex structure of biomass [64]. Biomass components mainly consist of carbohydrates, lignin, protein and fats [60]. The decomposition of these components in subcritical water conditions yield different products, but degradation mechanisms comprise the following steps [60]:

- depolymerization of the biomass;
- degradation of monomers (cleavage, dehydration, and decarboxylation reactions); and
- recombination of fragmented components.

Macromolecules in the structure of biomass first dissociate into water-soluble oligomers and monomers by hydrolysis. The monomers and oligomers may also undergo further degradation, re-polymerization or have their functional groups reduced [31]. Glucose monomers of cellulose are bonded to each other by β -(1–4) glycosidic bonds. These bonds lead to the formation of strong intramolecular and intermolecular hydrogen bonds. Water at high temperature and pressure breaks down this hydrogen bonded structure and causes the formation of glucose monomers. As a result of the decomposition of cellulose, glucose and other oligomers of cellulose may form. Some of these oligomers may be further hydrolyzed and converted into glucose. The hydrolysis of glucose takes place very quickly in hydrothermal media, and depending on the conditions, a wide range of products, including acetic acid, acetaldehyde, glyceraldehyde, glycolaldehyde, and furfural derivatives, can be formed [47]. Hemicellulose consists of a wide range of sugar monomers, such as xylose, mannose, glucose, and galactose, and may also have side chains. Due to its complex nature, hemicellulose does not have the same crystal structure and resistance as cellulose. It is therefore more conducive to hydrolysis, and can readily dissolve in water at 180 °C and higher temperatures [65]. Xylose from hemicellulose is found in water as a pyranose ring, a furanose ring or an open chain structure. Furfural may form from the pyranose ring state of xylose, whereas compounds such as glyceraldehyde, pyruvaldehyde, formic acid, lactic acid and acetol may form from its open chain structure [47]. Lignin, which is another component contained in the structure of the lignocellulosic materials, has a much more irregular structure and higher molecular weight than hemicellulose. As the density of water increases in a hydrothermal environment, hydrolysis increases, causing an increase in decomposition of lignin to its low molecular weight components [66,67]. Usually phenolic compounds form as a result of the hydrothermal degradation of lignin [68].

Although water behaves as both solvent and reactant, most organic compounds do not interact with water under normal conditions [64]. However, this changes when the temperature reaches approximately 250–350 °C when water molecules become involved in chemical reactions. Though most compounds within the raw material, including benzyl aryl ethers, benzonitriles, pyridinecarbonitriles, benzamides, and cyclohexyl phenyl compounds, are not thermally reactive, when the temperature increases to approximately 250 °C, they gain the capacity to react. Cyclohexyl phenyl compounds with bonded oxygen, sulfur and nitrogen atoms can dissociate to form methylcyclopentene with phenol, thiophenol or aniline at this temperature. Benzonitriles, pyridinecarbonitrile, benzamides and pyridinecarboxamides can also rapidly hydrolyze to ammonium carboxylates [64].

Various factors, such as temperature, pressure, reaction time, size of biomass particles, use of catalyst, and reaction medium, influence the yield and composition of resulting bio-oils [31]. In general, there is an increase in bio-oil yield up to approximately 300–350 °C; the gas product yield increases at higher temperatures (i.e., ≥ 350 °C). Although the products of hydrothermal liquefaction have lower oxygen content and thus, higher heating values compared with those from pyrolysis, bio-oils cannot be used directly as a fuel for transportation [69]. For a fuel to be used in transportation, it needs to have additional physical characteristics. These include high energy content, a good combustibility, and the ability to conveniently store in an effective manner [15]. The oxygen content of biomass is 40–60%, whereas high-quality fuels have an oxygen content of less than 1% [31]. A significant amount of biomass oxygen is removed by dehydration or decarboxylation reactions [60]. Though there is excess water in the reaction medium, dehydration reactions usually occur in hydrothermal media at high temperatures and pressures. Dehydration

reactions are accelerated by the catalytic effect of small amounts of Arrhenius acids (e.g., H_2SO_4) [47]. Decarboxylation reactions remove biomass oxygen as CO_2 , which has no calorific value. These reactions result in the formation of higher quality fuels by increasing the H/C ratio [31,47].

Bio-oils obtained as a result of a hydrothermal process can be improved and used instead of gasoline or diesel. Improvement procedures for obtaining high-quality liquid fuels from bio-oils can be conducted by physical (i.e., separation, extraction or solvent addition), chemical or catalytic means [70]. Hydrodeoxygenation is a bio-oil improvement method and is conducted at 300–600 °C under high pressure H_2 in the presence of a heterogeneous catalyst [69]. During hydrodeoxygenation, oxygen in the bio-oil reacts with H_2 to form water and saturated C–C bonds. In this manner, the energy content and the stability of the fuel is significantly increased.

Román-Leshkov et al. conducted a study on production of 2,5-dimethylfuran, a bio-based liquid fuel [15]. This study is schematically shown in Fig. 8. Variations in oxygen contents and boiling points of products obtained from the synthesis of 2,5-dimethylfuran from fructose are indicated. Additionally, research octane numbers (RON) and water solubilities of mono-oxygenated C_6 compounds are shown in comparison with ethanol. Light gray boxes in the figure indicate reactants, products and primary intermediate products. Dark gray boxes indicate byproducts and byproduct intermediates. In the first step of the study, 5-(hydroxymethyl) furfural (HMF) was obtained as a result of an acid-catalyzed dehydration of fructose. Because the normal boiling point of HMF is too high, it cannot be used as a liquid fuel for transportation. HMF was converted into 2,5-dimethylfuran in the presence of a copper–ruthenium (CuRu) catalyst by the hydrogenolysis of C–O bonds. Dehydration reactions were conducted at 180 °C and under a self-generated vapor pressure, while hydrogenolysis reactions were conducted at 220 °C and under an initial H_2 pressure of 6.8 bar. By the removal of 5 oxygen atoms from fructose, the formation of 2,5-dimethylfuran maintains a high energy density (30 kJ cm^{-3}), decreases the boiling point to a suitable value for liquid fuels, and achieves the lowest water solubility and the highest research octane number (RON) [15].

HMF, one of the products obtained by the hydrothermal liquefaction of carbohydrates, is not only used for obtaining compounds, such as dimethylfuran, used in the production of biofuels, but is also used for obtaining valuable compounds such as levulinic acid, 2,5-furandicarboxylic acid, 2,5-diformylfuran, dihydroxymethylfuran and 5-hydroxy-4-keto-2-pentenoic acid [71,72]. In Fig. 9, the synthesis of 5-(hydroxymethyl) furfural from carbohydrates and its conversion into substantial chemicals are schematically shown.

3.2.2.3. Separation and extraction of products. Separation and extraction procedures of the biomass products under hydrothermal conditions are important. There are various separation and extraction procedures for each type of product. Yuan et al. investigated hydrothermal liquefactions of biomass at 200, 220, 250, 300 and 310 °C [73]. After the HTL processing of biomass, gaseous products were vented, and liquefaction products were filtered under vacuum. The liquid portion contained water soluble products and analyzed for total organic carbon (TOC). The solid portion on the filter paper was extracted with tetrahydrofuran (THF) and analyzed by gas chromatography–mass spectrometry (GC–MS). Solid residue products (i.e., THF-insoluble compounds) were obtained by drying in an oven at 105 °C. The products were analyzed by a scanning electron microscope (SEM), a Fourier transform infrared spectrometer (FTIR) and an elemental analyzer. Kumar and Gupta obtained bio-crude from switchgrass under subcritical water conditions between

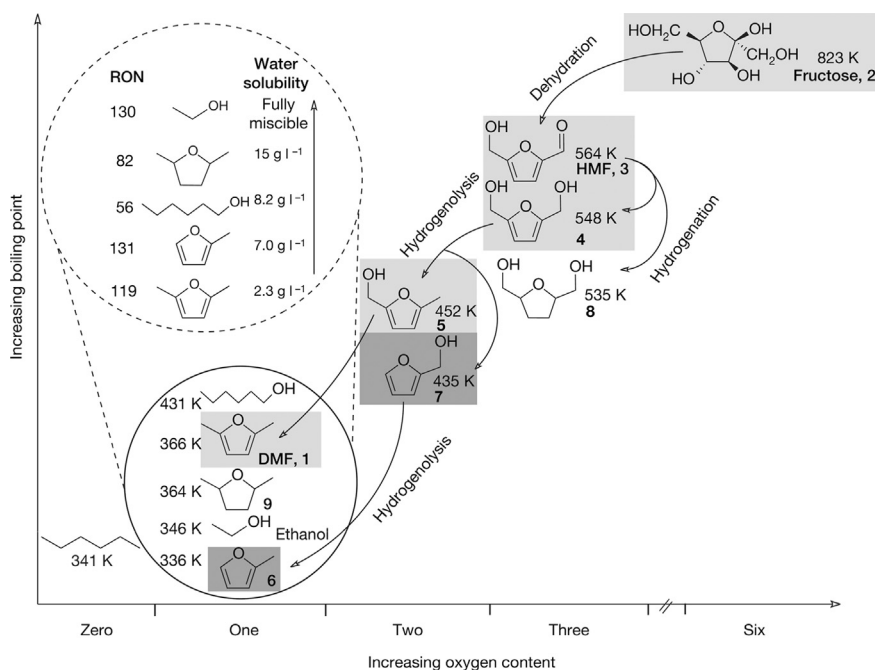


Fig. 8. Normal boiling points of representative C₆-hydrocarbons formed by removal of oxygen atoms from hexoses compared with the normal boiling point of ethanol. Compounds are as follows: 2,5-dimethylfuran (DMF) (1); D-fructose (2); 5-(hydroxymethyl)furfural (HMF) (3); 2,5-dihydroxymethylfuran (4); 2-methyl-5-hydroxymethylfuran (5); 2-methylfuran (6); furfural alcohol (7); 2,5-dihydroxymethyltetrahydrofuran (8); and 2,5-dimethyltetrahydrofuran (9). Reproduced from Ref. [15] with kind permission from the Nature Publishing Group.

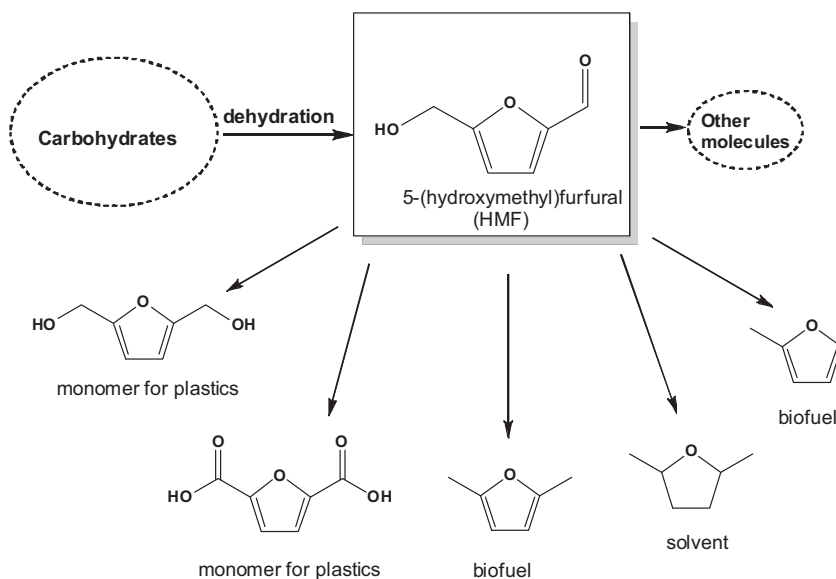


Fig. 9. Production of 5-(hydroxymethyl)furfural (HMF) from carbohydrates and its further derivatization to valuable chemicals (adopted from Refs. [71] and [72]).

235 and 260 °C [74]. They classified products as the aqueous phase, the solid precipitates and bio-char. After removing the suspended solids by centrifuge, aqueous phase samples were obtained and analyzed by TOC. Water soluble products were determined by a high performance liquid chromatography (HPLC) technique with refractive index detection. The determination of phenolic compounds was performed using GC–MS. Solid products were dried in an oven at 105 °C and analyzed for the carbohydrate composition. Bio-char products were analyzed by X-ray diffraction (XRD), FTIR, and SEM techniques. The subcritical/near critical liquefaction of woody biomass (Jack pine sawdust) was carried out at between 280 and 380 °C [75]. After the ventilation of gaseous products, solid and liquid products were filtered under reduced pressure. The water was completely removed from the liquid

portion using an evaporator at 85–90 °C, and water-soluble oil was obtained. The solid residue and reactor were washed with acetone prior to evaporation under reduced pressure; the resulting fraction was a heavy oil. The water-soluble oils and heavy oils were analyzed by elemental analysis. The heavy oils were analyzed using GC–MS. Solid residue products were analyzed by XRD. The hydrothermal treatment of biomass using different alkaline solutions (i.e., Na₂CO₃, K₂CO₃, Rb₂CO₃, Cs₂CO₃, NaOH, KOH, LiOH, RbOH, and CsOH) was studied at 280 °C for 15 min [76–78]. Liquid and solid products were acidified by the addition of hydrochloric acid, which helped complete the separation of liquid and solid products. Two different solvent extractions, diethyl ether and ethyl acetate, were used to maximize the recovery of bio-oils. Liquid products were extracted with diethyl ether, a non-polar solvent. Then, the remaining water was extracted

with ethyl acetate, a polar-aprotic solvent. The first fraction of bio-oil products (oil 1) were recovered by removing the ether fraction. The second fraction of bio-oil products (oil 2) were obtained after removing the solvent (ethyl acetate). The amount of bio-oil obtained from the ethyl acetate extraction was quite low. Tar-like products (oil 3) were obtained from the extraction of solid products with acetone using a Soxhlet extraction. Solid residue products were obtained by drying the acetone-insoluble fraction at 105 °C. Oil products were analyzed by GC–MS. The hydrothermal treatment of microalgae was carried out at temperatures between 175 and 450 °C with residence times of 5–60 min [79]. First, dichloromethane (DCM) was applied for the extraction of slurry. Vacuum filtration was applied to separate solid and liquid products. After separation of DCM from aqueous phase, DCM was removed by evaporation and the resulting product was called as oil. Aqueous phase was evaporated at 70 °C for 24 h. After removing the water, this water-soluble organics fraction was quantified. The solid residue after filtration was dried at 105 °C for 24 h to remove any remaining solvent and subsequently quantified. Oils were analyzed using GC–MS, Gel Permeation Chromatography (GPC) technique and elemental analysis. Solid residues were analyzed using SEM. The hydrothermal liquefaction of marine macroalgae was carried out at temperatures of 220–320 °C with a reaction time of 30 min [80]. After the ventilation of gaseous products, DCM was added to the reaction mixture and two phases were separated. The DCM phase was filtered and evaporated under reduced pressure to obtain bio-oil. The solid residues, DCM-insoluble products, were dried at 105 °C for 12 h. The remaining water-soluble, aqueous phase products after phase separation were evaporated at 65 °C for 12 h. Bio-oils were analyzed by GC–MS, FTIR, nuclear magnetic resonance (NMR) spectrometry and an elemental analyzer. The solid residue products were analyzed by FTIR. Water soluble products were washed with methanol to remove water soluble salts and analyzed by GC–MS. The hydrothermal treatment of crude algal oils was carried out at 260 °C for 30 min [81]. After the hydrothermal process was completed, the pH of the products was adjusted to pH 4 with sulfuric acid. The acidified product was heated to 60 °C for 30 min. After acidification, a solvent extraction was carried out with heptane at 70 °C for 30 min with constant mixing. After 30 min, the mixing was stopped, and the phase separation occurred at room temperature. Upon removal of solvent under reduced pressure, bio-oils were obtained. The obtained crude algal oils were upgraded at 350, 400 and 450 °C for 60 min. The oils were analyzed using elemental analysis, GC–MS, and a gas chromatograph-flame ionization detector (GC–FID) to obtain a simulated distillation curve. In another study, the hydrothermal liquefaction of algal biomass was carried out at 350 °C for 60 min and the effect of solvent polarity on bio-oil yields and extraction compositions was investigated [82]. After hydrothermal algal biomass processing, gas products were released. Then, 10 mL of nonpolar (hexadecane, decane, hexane, and cyclohexane) and polar solvents (methoxycyclopentane, chloroform, and dichloromethane) was added into the reactor, and the reactor was slowly rotated (10 rpm) at room temperature for 120 min. This enables the maximum contact between the solvent and reactor wall, and led to the recovery of bio-oil products. The organic, aqueous and solid phases were separated via centrifugation. The highest gravimetric yields of bio-oil were obtained for the hexadecane and decane extractions. However, bio-oils obtained with polar solvents, such as chloroform and dichloromethane, contained the highest amounts of carbon content. The compositions of the bio-oils were analyzed by GC–MS.

As is well-known, the selective extraction of chemicals from bio-oil is difficult because bio-oil is a complex mixture of organic compounds. The extraction of phenols from tar obtained from the pyrolysis of eucalyptus plants was studied [83]. It was shown that the selective extraction of phenols from wood tar is possible via a liquid–liquid extraction using alkaline solvents. Minowa and

co-workers studied the methanol-mediated extraction of wood tar [84]. It was shown that this extraction helped to selectively recover phenolic compounds from wood tar.

The separation of liquids and solids is difficult when alkaline solutions were used as catalysts in hydrothermal processing [2]. However, this problem can be overcome by the addition of hydrochloric acid [77,78,85]. Otherwise, the separation of liquid and solid products cannot be completed; the solid residues would contain a high proportion of the catalyst metal ions and the liquid fraction may retain solid products [2]. The optimum separation and extraction procedure for products obtained from hydrothermal biomass processing [8] is shown in Fig. 10.

3.2.2.4. Analysis of products

3.2.2.4.1. Mass spectrometry analysis. Mass spectrometry is a useful technique to quantify atoms or molecules and to determine unknown compounds in a sample; compounds are converted into gaseous ions, and their mass-to-charge ratios (m/z) are measured. The following mass spectrometric methods are commonly used for the determination of organic compounds in a sample: mass–mass spectrometry (MS–MS), liquid chromatography–mass spectrometry (LC–MS), and gas chromatography–mass spectrometry (GC–MS). The most preferred analytic technique for the analysis of bio-oils from the HTL of biomass is GC–MS. However, GC–MS has some limitations, including coke formation in the injector port and the inability to determine non-volatile compounds in bio-oils.

Various compounds in bio-oils from the HTL of biomass have been identified by GC–MS. It is possible that the formation or non-formation of some compounds is dependent on the type of biomass and experimental conditions (i.e., temperature, pressure, type of catalyst, and biomass/water ratio). The composition of bio-oils from the hydrothermal liquefaction of biomass yields a broad range of compounds consisting primarily of oxygenated hydrocarbons. Key compounds determined by GC–MS produced from the hydrothermal liquefaction of woody biomass are as follows [54,62,86]: phenols, benzenediols, acids, ketones, vanillin, and furfurals. Some of the following key compounds are produced from the hydrothermal liquefaction of algal biomass [87,88]: fatty acids, indoles, pyrroles, alkanes, alkenes, pyridinols, and acetyl furans. It is quite difficult to obtain a high yield of a specific compound [5]. However, when processing a single biomass component or bio-based model compounds, a target compound can be obtained at high yields. Although the determination of the relative concentration of each compound in bio-oils by GC–MS is acceptable, the use of GC–FID with an internal standard is preferred for the quantification of compounds from the HTL of biomass. Due to reasons stated earlier, GC–MS is commonly used as an analytical technique for the identification and determination of relative concentrations of compounds in bio-oils. A representative total ion chromatogram for bio-oils obtained from the HTL of beech wood is shown in Fig. 11 [54].

3.2.2.4.2. Fourier transform infrared (FTIR) spectrometry analysis. FTIR is a technique to determine functional groups in the raw material, bio-oil and bio-char. Some representative FTIR spectrums for bio-oils and bio-chars obtained from the hydrothermal liquefaction of woody biomass are shown in Fig. 12 [89]. FTIR spectra of the products from the non-catalytic and catalytic runs with colemanite were similar. The peak between 3300 and 3600 cm^{-1} is assigned to O–H stretching vibrations. The peak at between 2870 and 2960 cm^{-1} represent C–H stretching vibration. The sharp peak at between 1680 and 1840 cm^{-1} is attributed to the C=O functional group. The peak at 1230 cm^{-1} corresponds to C–O bending vibrations. The peaks observed between 1500 and 1600 cm^{-1} are mainly attributed to aromatic C=C groups. The peaks observed between 650 and 900 cm^{-1} represent C–H

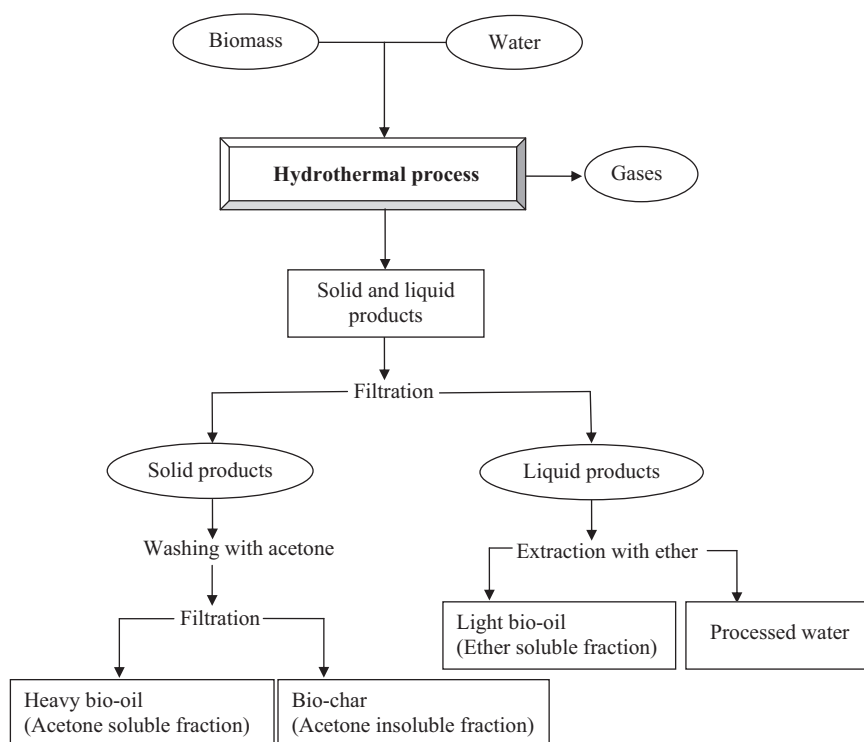


Fig. 10. The procedures for separation and extraction of the products obtained from hydrothermal conversion of biomass (adopted from Ref. [8]).

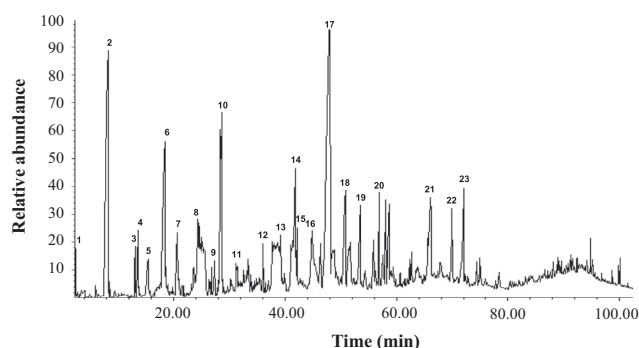


Fig. 11. TIC of bio-oil obtained from hydrothermal liquefaction of beech wood at 300 °C. Reproduced from Ref. [54] with kind permission of the Elsevier Publishing Group. (1) Acetic acid; (2) Furfural; (3) 2-Methyl-2-cyclopenten-1-on; (4) 1-(2-Furanyl)-ethanone; (5) 2,5-Hexanedion; (6) 5-Methylfurfural; (7) Phenol; (8) 2-Hydroxy-3-methyl-2-cyclopenten-1-on; (9) 2-Methylphenol; (10) 2-Methoxyphenol; (11) 3-Ethyl-2-hydroxy-2-cyclopenten-1-on; (12) 3,4-Dimethylphenol; (13) 1,2-Benzenediol; (14) 5-(Hydroxymethyl)furfural; (15) 4-Ethyl-2-methoxyphenol; (16) 4-Methyl-1,2-benzenediol; (17) 2,6-Dimethoxyphenol; (18) Vanillin; (19) 3-Hydroxy-4-methoxy-benzoic acid; (20) Butylated hydroxytoluene; (21) 4-Hydroxy-3,5-dimethoxybenzaldehyde; (22) 1-(4-Hydroxy-3,5-dimethoxyphenyl)ethanone; and (23) 1-(2,4,6-Trihydroxyphenyl)-2-pentanone.

vibrations in an aromatic structure. FTIR spectra show that aromatic contents in bio-chars are high. This situation can be explained by the aromatic core of the hydrothermal carbon (HTC).

3.2.2.4.3. Elemental analysis. Elemental analysis is used to determine elemental compositions (i.e., carbon, hydrogen, oxygen, nitrogen and sulfur) of the raw material, bio-oils and bio-chars. It also provides the atomic ratios of O/C and H/C. The O/C ratio is an important criterion for estimating the degree of de-oxygenation taking place during the HTL of biomass. The H/C ratio can provide clues regarding the aromatic content of bio-oils and bio-chars; if the H/C ratio of bio-oils and/or bio-chars is high, then the aromatic content is low. Generally, H/C ratios of bio-chars produced from hydrothermal liquefaction are high, which indicates higher aromatic content in bio-chars than that of the raw material. Heating

values of bio-oils and bio-chars can be determined from elemental compositions using the Dulong Formula: $\text{HHV} = 0.338\text{C} + 1.428(\text{H} - \text{O}/8) + 0.095\text{S}$ [89].

3.2.2.4.4. Nuclear magnetic resonance (NMR) analysis. Nuclear magnetic resonance (NMR) can be used for the qualitative analysis of functional groups in bio-oils from the HTL of biomass. ^1H and ^{13}C NMR are commonly used for the characterization of bio-oil from the HTL of biomass [77,90]. In general, characteristic peaks of ^1H NMR are as follows: the peaks between 6 and 8 ppm are assigned to aromatic protons. The peak observed at approximately 4 ppm is assigned to protons of the methoxy group ($-\text{OCH}_3$). The peaks observed between 0.8 and 3.0 ppm represent the protons of alkyl groups ($-\text{CH}_2$ and $-\text{CH}_3$). The peaks between 9 and 10 ppm show aldehyde protons. In ^{13}C NMR characteristic carbon chemical shifts in bio-oils are as follows: the peaks between 0 and 40 ppm represent alkyl groups ($-\text{CH}_2$ and $-\text{CH}_3$), the peaks between 50 and 60 ppm are assigned to methoxy carbons ($-\text{OCH}_3$), the peaks between 100 and 160 ppm represent aromatic carbons ($\text{Ar}-$), the peaks between 170 and 180 ppm are indicative of aldehyde carbons, and the peaks between 160 and 185 ppm are assigned to carboxylic acid carbons ($\text{COOH}-$). Because bio-oils from the HTL of biomass consist of a wide range of compounds, chemical shifts of functional groups may be affected.

3.2.2.5. Recent works (2011–2013). An impressive amount of scientific studies related to conversion of biomass in hydrothermal media has been reported in the literature. In recent years, hydrothermal liquefaction process has been mainly applied to algal biomass, which is a good example for wet biomass. Toor et al. used two different algal biomasses, *Nannochloropsis salina* and *Spirulina platensis*, for the liquefaction of biomass under sub-critical water conditions (i.e., 220–375 °C, 20–255 bar) [91]. Biocrude yields ranged from 30 to 38 wt% for *S. platensis* and from 24 to 46 wt% for *N. salina*. To extract polysaccharides, Chakraborty et al. performed the hydrothermal liquefaction of *Chlorella sorokiniana* between 140 and 200 °C [92]. Approximately 90% of polysaccharides were

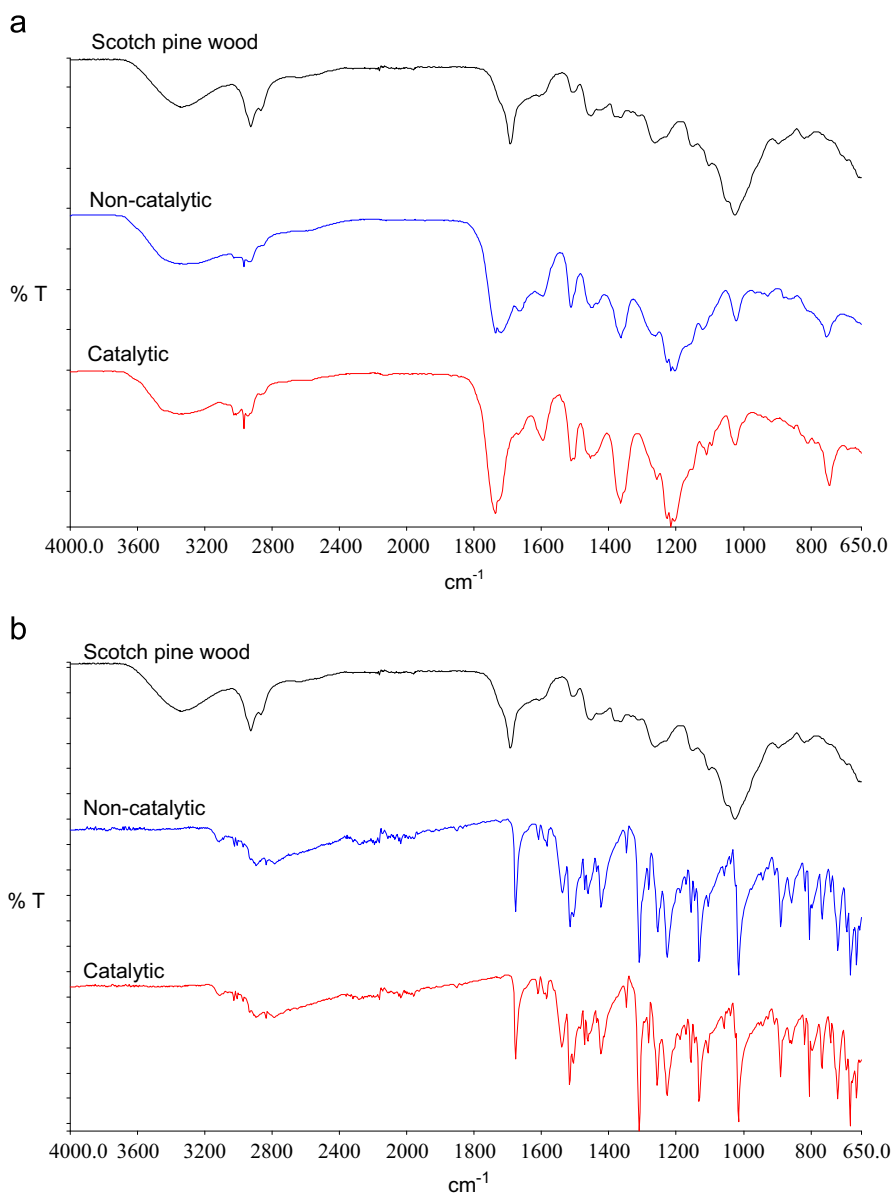


Fig. 12. (a) FTIR spectra of raw material and bio-oils from hydrothermal liquefaction of Scotch pine wood at 300 °C. (b) FTIR spectra of raw material and bio-chars from hydrothermal liquefaction of Scotch pine wood at 300 °C (taken from Ref. [89]).

extracted containing an α -glucan. Miao and co-workers extracted bio-oils and polysaccharides from *C. sorokiniana* with a two-step sequential hydrothermal liquefaction process [93]. The maximum polysaccharide yield was obtained at 160 °C, 20 min and a 1:9 biomass/water ratio. Valdez et al. liquefied *Nannochloropsis sp.* under sub- and supercritical water conditions at different temperatures (250–400 °C), residence times (10–90 min), and biomass loadings (5–35 wt%) [94]. The yields of light and heavy fractions were mainly affected by the hydrothermal liquefaction temperature. The highest bio-crude yield of 50 wt% was obtained at 300 °C. The hydrothermal liquefaction of four different microalgae was carried out at 300 and 350 °C [95]. The bio-crude yields ranged from 27 to 47 wt% depending on the type of microalgae. In another study, the hydrothermal liquefaction of three different biomass types, *Spirulina* algae, swine manure, and digested sludge, were investigated at 300 °C, 10–12 MPa, and a residence time of 30 min [96]. Bio-crude yields ranged from 9.4 to 32.6 wt% and heating values were found to be similar (i.e., 32.0–34.7 MJ/kg). Acetic acid was produced from microalgae under hydrothermal conditions at 300 °C for 15 s with H_2O_2 [97]. The highest acetic acid yield was

found to be 14.9% (based on a carbon base) and was obtained at the following conditions: 300 °C, 80 s and with a 100% hydrogen peroxide (H_2O_2) supply.

Lignocellulosic biomass and its components, and some bio-wastes have been also used under hydrothermal liquefaction conditions. The hydrothermal liquefaction of lignin compounds was studied at temperatures of 370 and 390 °C at 25 MPa and with residence times of 5 and 40 min [98]. A reaction pathway followed the fragmentation and condensation reactions. In a study related to production of bio-oil from the hydrothermal liquefaction of separated dairy manure was carried out at 250, 275, 300, 325 and 350 °C with and without Na_2CO_3 for a residence time of 15 min [99]. The highest bio-oil yield (in the acetone-soluble fraction) was found to be 24 wt% at 350 °C using 1 g of Na_2CO_3 . Moller et al. performed a microwave-assisted hydrothermal conversion of fructose and glucose in subcritical water between 180 and 250 °C [100]. 5-(Hydroxymethyl) furfural (HMF) was a major product from the conversions of fructose and glucose. Yin et al. obtained gasoline hydrocarbons from the hydrothermal liquefaction of cellulose at 300 °C for 15 min with in situ hydrogen in the

presence of aluminum oxide-supported platinum catalysts [101]. The yields of alkanes were strongly affected by the pH of the initial hydrothermal media. Hammerschmidt et al. performed the hydrothermal liquefaction of yeast with excess hydrogen and K_2CO_3 between 330 and 450 °C at pressures between 20 and 32 MPa with residence times from 1 to 30 min [102]. The yield of the oil phase was quite high and reached 51.4%. The production of bio-oil from duckweed between 270 and 380 °C with residence times of 10–120 min with and without K_2CO_3 was carried out by Duan and co-workers [103]. The highest biocrude yield (30 wt%) was obtained at 340 °C and 60 min. The formation of coke from the hydrothermal processing of glycerol and glucose was investigated at different temperatures (300–450 °C), initial pressures (2–7 MPa) and residence times (0–120 min) [104]. The maximum coke formation was 66% for glucose and 19% for glycerol. Tekin et al. recently studied the liquefaction of woody biomass under hydrothermal conditions at 250, 300 and 350 °C with a residence time of 0 min [62,86,105]. They used a wide range of boron catalysts in the hydrothermal liquefaction process. The effect of catalysts (i.e., colemanite, sodium perborate monohydrate, disodium octaborate tetrahydrate and boric acid) and temperature were tested for the process. All tested catalysts, except boric acid, effectively increased bio-oil yields [62,86,105]. The optimal temperature was 300 °C for the highest bio-oil yield. The tested catalysts were effective for different types of wood samples.

Hydrothermal processing under subcritical and supercritical conditions was also used for upgrading bio-oils [106–109]. Crude algal bio-oil was upgraded using carbon-supported palladium catalysts (at different metal loadings) in supercritical water at 400 °C and 3.4 MPa with H_2 [106]. It was shown that longer residence times and higher catalyst loadings increased the heating value of treated bio-oils, but not the treated oil yield. The upgraded bio-oils had low boiling compounds and mainly consisted of alkane derivatives. In another upgrading study, Duan et al. upgraded crude algal oil using platinum/gamma alumina in supercritical water in the absence and presence of formic acid at 400 °C for 1 h [109]. The product yields were largely affected by water density, catalyst amount, and formic acid amount. A higher catalyst loading produced a lower yield of upgraded bio-oil but of higher quality.

3.2.2.6. Hydrothermal gasification. Hydrothermal gasification is a process in which biomass thermochemically decomposes into its liquid components and then to its gaseous components in pressurized hot water [6,110]. Water acts not only as a solvent but also as a reactant under near critical/supercritical conditions. Biomass rapidly undergoes hydrolysis under subcritical and supercritical conditions. Under supercritical water conditions, the dissolution of reactive species caused by decomposition of biomass prevents the formation of bio-char, thereby ensuring a high gas yield [111].

Hydrothermal gasification is most widely used for producing methane and hydrogen gas [31]. The process can be divided into three sections according to the desired product [47]:

- the production of a hydrogen-rich gas product (without a catalyst at temperatures above 500 °C or using a non-metallic catalyst);
- the production of a methane-rich gas product (using a catalyst between the critical temperature and 500 °C); and
- the production of a gas product using a catalyst at subcritical temperatures.

Biomass decomposition chemistry is very complex. During hydrothermal gasification, biomass decomposes into lower molecular

weight compounds by hydrolysis reactions. Other than the hydrolysis reaction, many other reactions, such as thermal decomposition, water-gas-shift reaction and methanation, also take place. High temperatures break the bonds of components in the biomass enabling the formation of gases, such as H_2 , CH_4 , CO and CO_2 . A catalyst is necessary during hydrothermal gasification carried out at sub-critical temperatures [67,112]. For this purpose, nickel, ruthenium, rhodium and alkaline salts are commonly used as catalysts [111]. At high temperatures (i.e., 500–800 °C), free radical mechanisms are governed by pyrolysis and water-gas-shift exchange reactions form H_2 gas [31,113]. Hydrogen-rich gas products can be achieved by ensuring the near complete conversion of biomass in supercritical water at temperatures of approximately 600 °C. Carbon contained in the biomass is mainly converted into CO_2 . The effect of high temperatures (i.e., 500–700 °C) on gas product compositions and yield is rather high, while the effects of pressure at supercritical conditions are negligible [47].

In a study concerned with the gasification of glucose in supercritical water at 480–750 °C and 28 MPa, the yield of H_2 gas was reported to increase with increasing temperatures above 660 °C [113]. Though CO production reached its highest levels at this temperature, CO production subsequently decreased with increasing temperature due to the very high rate of the water-gas-shift reaction [31,113]. However, at high glucose concentrations, the rate of gasification decreased. To avoid this, activated carbon was used as a catalyst, and it was reported that glucose was subsequently completely converted into a hydrogen-rich gas [114].

Lignin in biomass is broken down to form lower molecular weight phenolic compounds in hydrothermal media [31]. Elimination reactions result in the formation of formaldehyde, which undergoes condensation reactions with alkyl phenols. Consequently, alkyl phenols polymerize and form higher molecular weight compounds in which formaldehyde acts as a cross-linking agent. Therefore, the presence of lignin increases the formation of bio-char but reduces the gas yield [31,115,116]. However, cellulose and lignin can be completely gasified to give CH_4 and CO_2 under supercritical conditions using ruthenium catalysts [67].

Hydrothermal gasification has advantages in that it can be applied to wet biomass, has high thermal efficiencies, produces hydrogen-rich products at low CO concentrations, and produces less soot and tar [117]. Resulting products have a very wide range of applications in electricity generation, fuel cells, and chemical synthesis [118].

3.2.2.7. Hydrothermal carbonization (HTC). Hydrothermal carbonization is a relatively new thermochemical conversion process that converts biomass to valuable products. This process is an environmentally friendly and inexpensive technique. Biomass is treated in water under mild temperatures (≤ 200 °C) and pressures for several hours [119]. This process requires lower energy expense than conventional carbonization and allows for a higher product yield in less time [120]. Its advantages include a low carbonization temperature, the aqueous phase synthesis, the use of inexpensive, renewable materials as sources of carbon (e.g., carbohydrates and derivatives thereof or raw biomass), and the use of remarkable chemicals such as nanoparticles or functional monomers in the structure [120].

Various studies have been conducted to convert carbohydrates, cellulose, and other biomass into carbon-rich materials by hydrothermal carbonization [9,120–125]. Hydrothermal carbonization reactions, in which carbohydrates are used as the source of biomass, take place in three important steps, which are [119]:

- the dehydration of carbohydrates into 5-hydroxymethyl furfural or furfural,

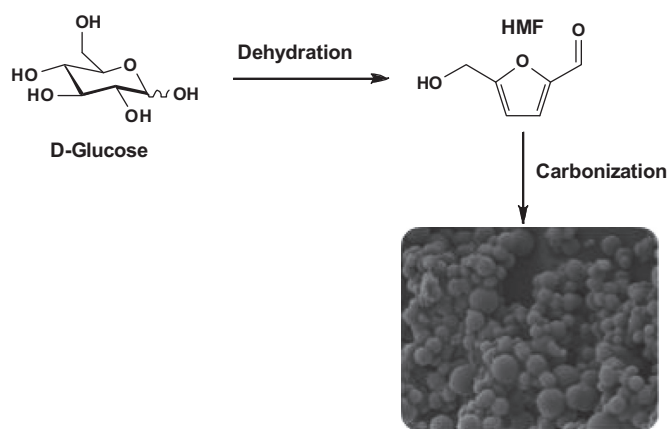


Fig. 13. Proposed reaction mechanism of hydrothermal carbonization from D-glucose.

- polymerizations to form polyfurans, and
- carbonizations via intermolecular dehydration.

Fig. 13 shows the proposed reaction mechanism for hydrothermal carbonization of D-glucose. Hydrothermal carbons derived from carbohydrates are in the form of spherical micron-sized particles with multiple polar functional groups. With these functional groups on the surface, the product can become more hydrophilic and easily disperse in water. Sizes of final particles vary depending on the carbonization time and the precursor concentration. Thus, carbons obtained by hydrothermal carbonization have their own characteristics. Studies on hydrothermal carbonization continues to increase as its applicability to such fields as nanotechnology and materials science increases [120].

3.2.3. Combustion

Combustion is an exothermic process in which carbon, hydrogen, and nitrogen within the biomass react with oxygen in the air. This method is the simplest and most commonly used method in which biomass is used to generate heat and electrical energy [37]. Energy content, or heating value of biomass, is an important factor and is defined as the heat released during combustion under specific conditions [22]. The amount of heat released during combustion depends on the carbon content, ash content, moisture content, and conversion rate of the biomass. The heating value of a biomass increases with an increasing carbon content of the biomass. This can be explained by the fact that the energy value of the carbon–carbon bond is higher than those of the carbon–oxygen and carbon–hydrogen bonds [3,22]. In woody biomass with an ash content of less than 1%, the heating value is approximately 20 MJ kg^{-1} , and each 1% increase in ash content results in a loss of approximately 0.2 MJ kg^{-1} . For biomass with high moisture content, a large part of the heat released is used to evaporate water in the structure. Even when the moisture content exceeds 90%, the amount of energy required to evaporate water exceeds the heating value of the raw material. When the moisture content of the combustible raw material is high, they are more often used in combination with natural gas or other fuels [22].

4. Conclusion

This review discussed the hydrothermal processing of biomass to obtain bio-oil, bio-gases and bio-carbon. Biomass is one of most important renewable energy sources. The hydrothermal processing of biomass can be divided into three methods: liquefaction, gasification and carbonization. Based on the target product, the

appropriate method is chosen. As is well-known, the physico-chemical properties of subcritical and supercritical water are different from those of ambient water, which makes it an excellent solvent and reaction medium. Although the process has some drawbacks, such as the ability to handle large volumes of water and to use complex and expensive reactors, it is still a prominent way to utilize biomass due to being suitable for any type of biomass and its ability to operate at moderate temperatures and pressures. Unlike other thermochemical processes, the separation, extraction and analyses of the biomass products under hydrothermal conditions are important and should be performed carefully.

In future applications, hydrothermal biomass processing to produce bio-oil, bio-gas and bio-carbon will take place in industrial practice. A combination of hydrothermal biomass processing with other processes will help to feasibly develop quality products.

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